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(54) **SUPERIOR PILLARED CLAY CATALYSTS
FOR SELECTIVE CATALYTIC REDUCTION
OF NITROGEN OXIDES FOR POWER
PLANT EMISSION CONTROL**

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1999.

(51) Int. Cl.⁷ **B01J 21/16**

(52) U.S. Cl. **502/84**

(58) Field of Search 502/80, 84; 423/239.1

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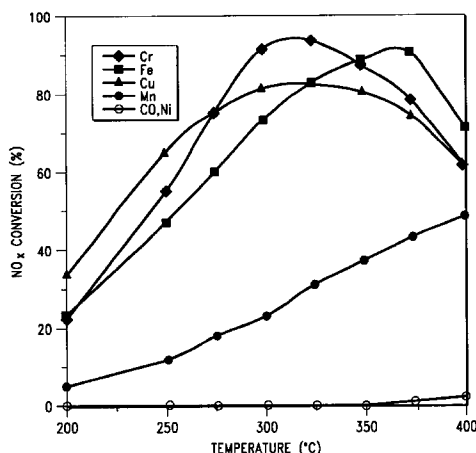
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(57) **ABSTRACT**

The present invention provides a catalyst for selective catalytic reduction of nitrogen oxide compounds with ammonia comprising a composition of one or more pillared interlayered clays, one or more metal ions exchanged with the pillared interlayered clays, and one or more promoter ions exchanged with the pillared interlayered clays. Specifically, the pillared interlayered clay (PILC) catalysts of the present invention include Fe³⁺, Cr³⁺, Mn²⁺, Co²⁺, Cu²⁺, and Ni²⁺ exchanged Al₂O₃-PILC, TiO₂-PILC, ZrO₂-PILC or SiO₂-PILC catalysts. The promoters include Ce, La, Pr, Th and Nd. These pillared clay catalysts of the present invention show remarkable activity for the SCR reaction.

12 Claims, 4 Drawing Sheets



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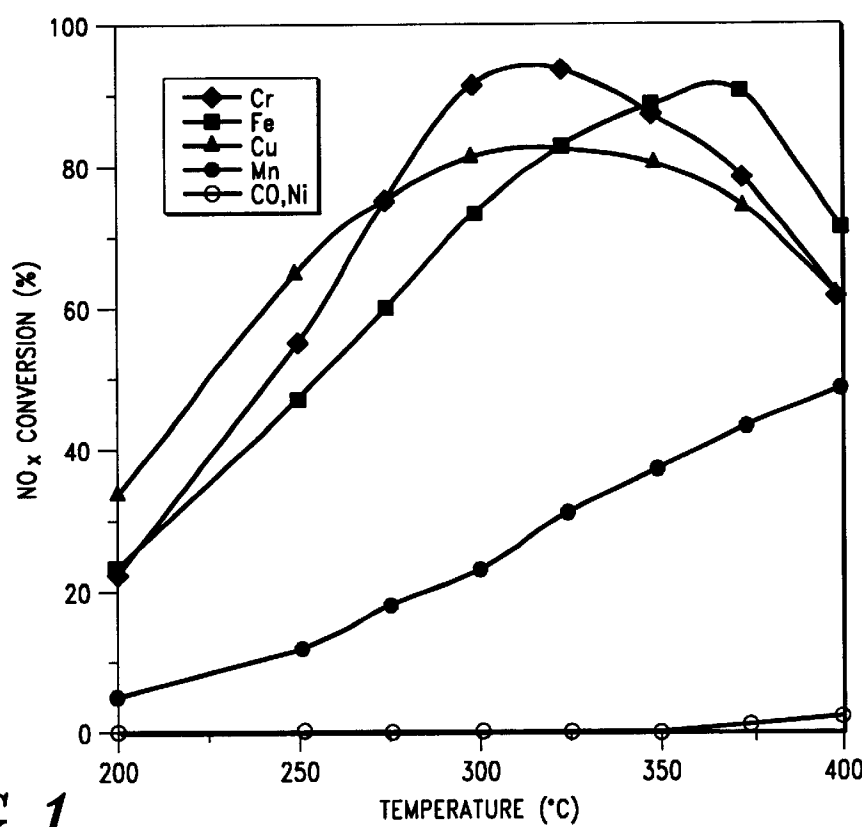


FIG. 1

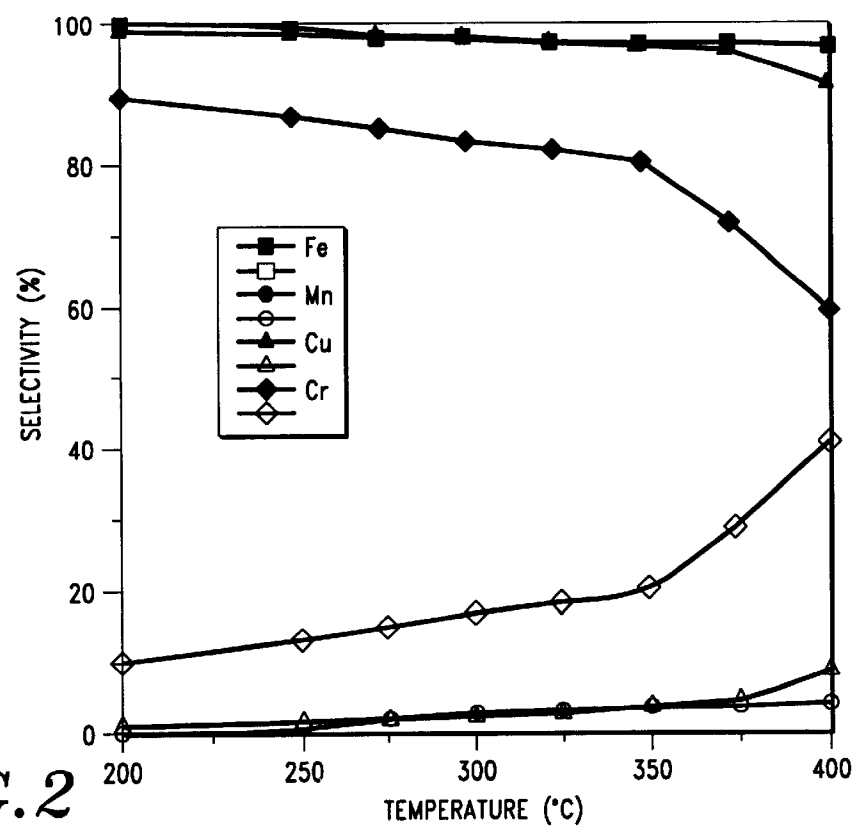


FIG. 2

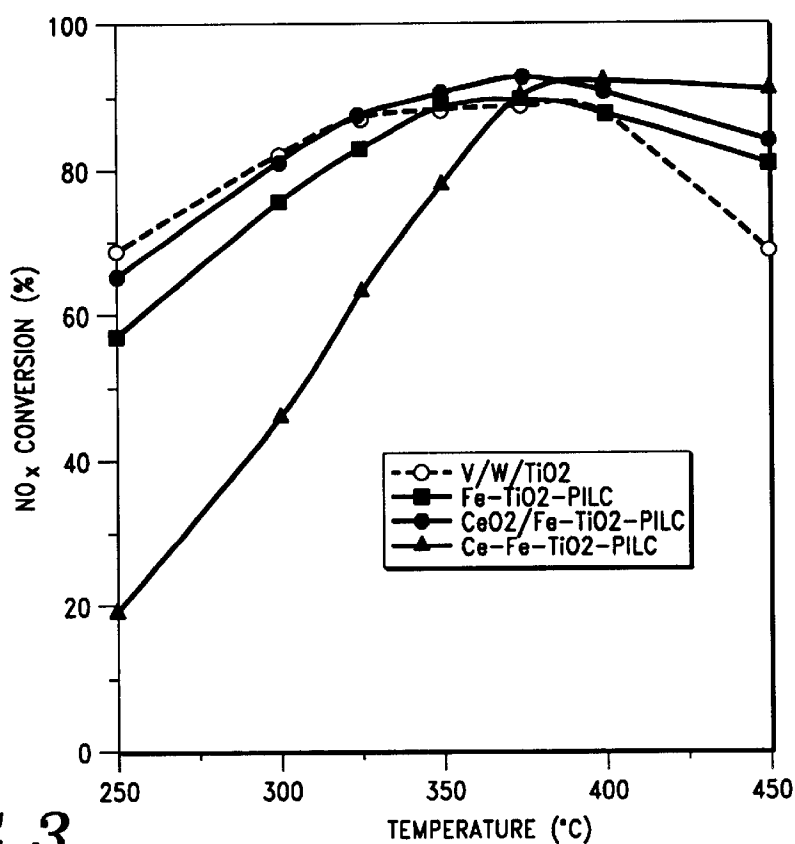


FIG. 3

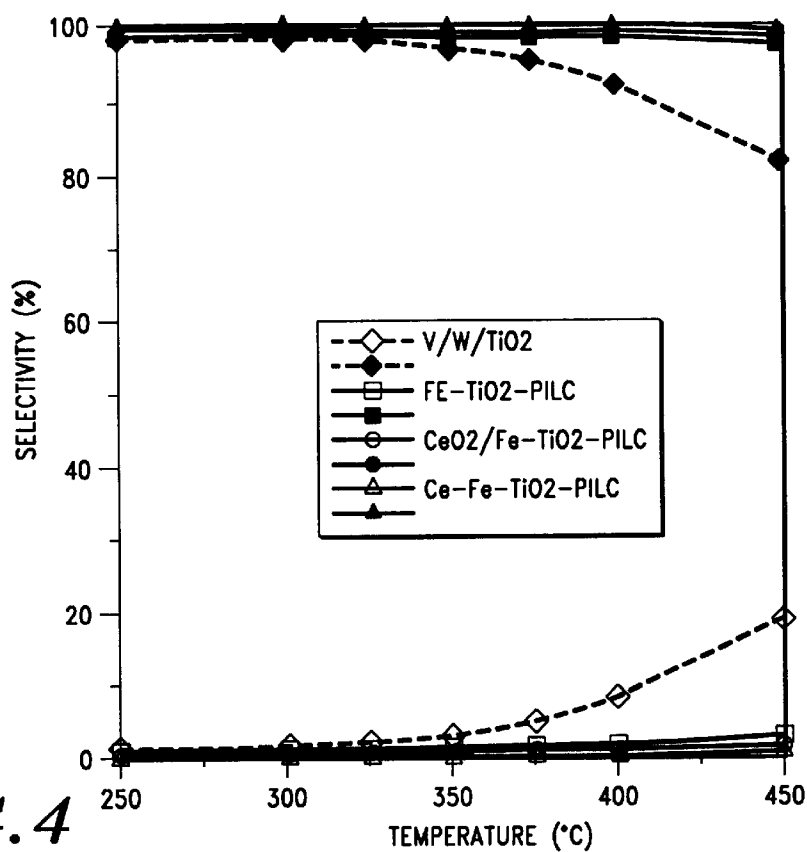


FIG. 4

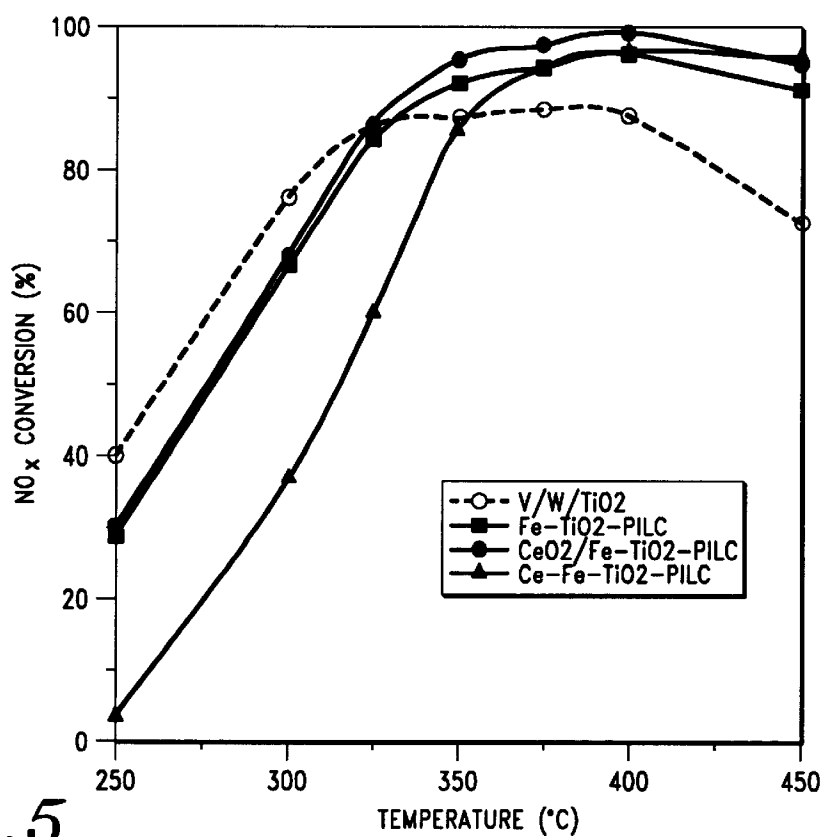


FIG. 5

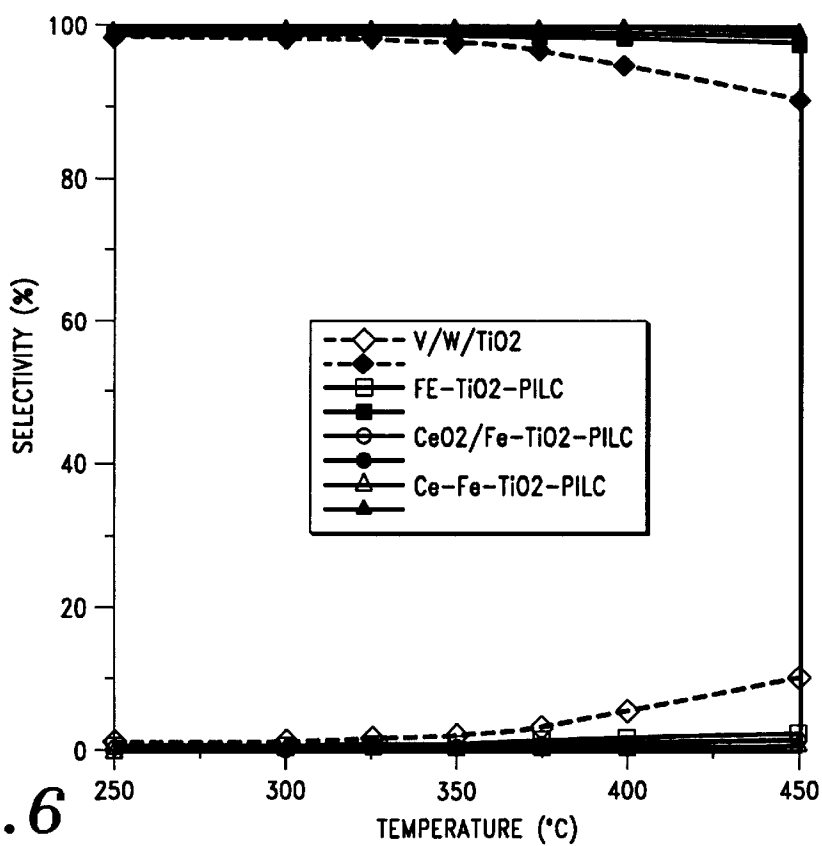


FIG. 6

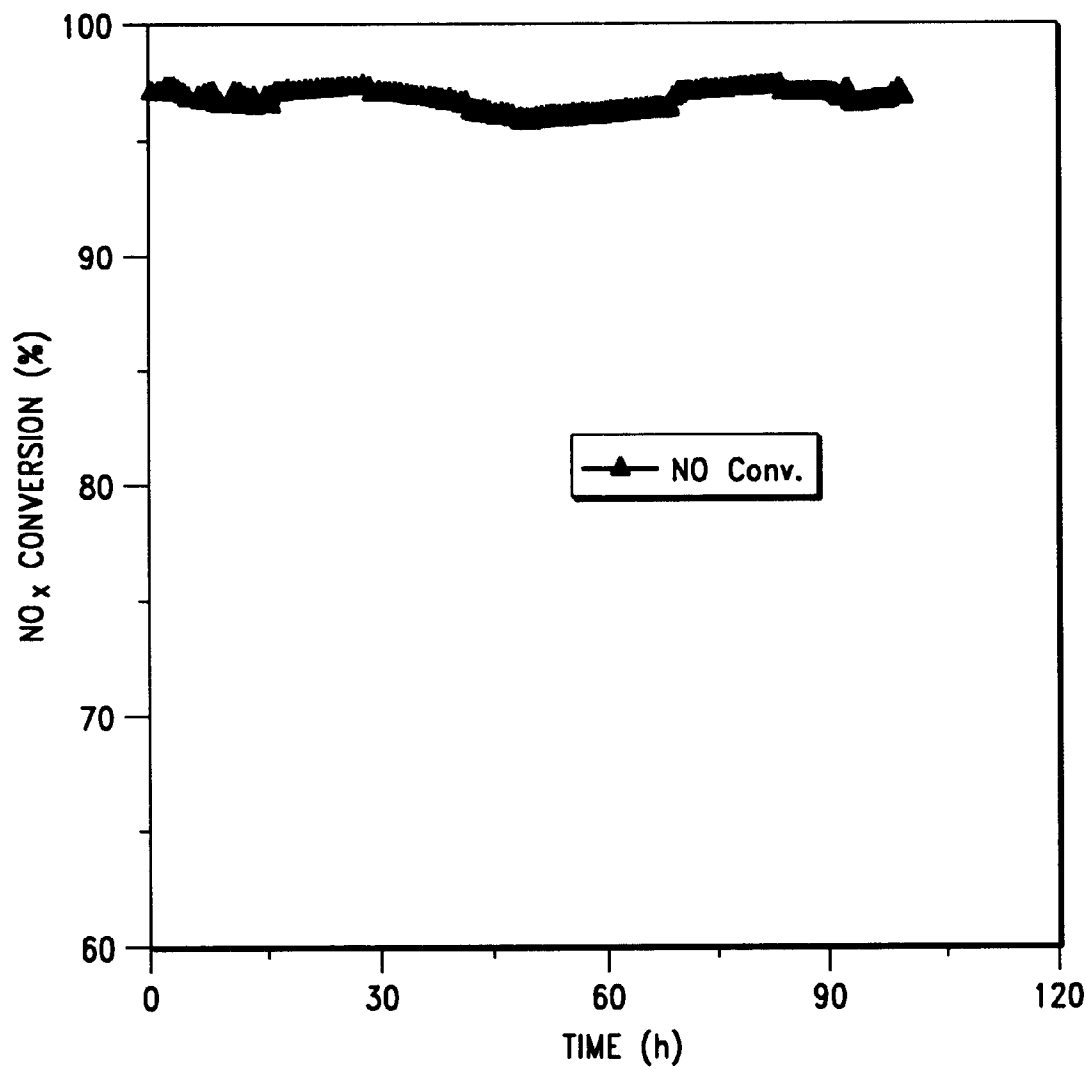


FIG. 7

SUPERIOR PILLARED CLAY CATALYSTS FOR SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES FOR POWER PLANT EMISSION CONTROL

RELATED APPLICATIONS

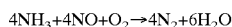
This application claims priority to U.S. Provisional Patent Application, Serial No. 60/156,263 filed Sep. 27, 1999, the entire disclosure of which is hereby incorporated by reference.

FIELD OF THE INVENTION

This invention relates in general to the controlling of nitrogen oxide (NO_x) emissions from fossil-fuel power plants. More particularly, the invention relates to a catalyst composition for controlling nitrogen oxide emissions from fossil-fuel power plants by selective catalytic reduction (SCR) with ammonia using pillared clay catalysts.

BACKGROUND OF THE INVENTION

Nitrogen oxides (NO, NO₂, and N₂O, collectively referred to as "NO_x") present in the exhaust gases from combustion of fossil fuels, continues to be a major source for air pollution. Nitrogen oxides contribute to photochemical smog, acid rain, ozone depletion and greenhouse effects. As a major cause of acid rain, nitrogen oxides additionally contribute to the pollution of water and soil. The current technology for reducing nitrogen oxides emissions from power plants is by selective catalytic reduction (SCR) of NO_x (where x is 1 to 2) with ammonia in the presence of oxygen, to form nitrogen and water. The overall reaction is as follows:



Many catalysts have been reported to be active for this reaction, such as vanadia and other transition metal oxides (e.g., V₂O₅, CuO, Fe₂O₃, Cr₂O₃, Fe₂O₃—Cr₂O₃, Nb₂O₅, and the like), pillared clays and zeolite-type catalysts. For example, in the SCR reaction, a vanadia catalyst V₂O₅+WO₃ (or MoO₃) supported on TiO₂ is commonly used as commercial catalysts. The mechanism of the reaction on the vanadia catalysts has been studied extensively and is reasonably understood although several different mechanisms have been proposed. Although the SCR technology based on vanadia catalysts has been commercialized, problems with this approach still remain. For example, the vanadia catalyst promotes high activity for the oxidation of SO₂ to SO₃, promotes formation of N₂O at high temperatures, and is toxic. The formation of SO₃ is undesirable because it reacts with NH₃ and H₂O to form NH₄HSO₄, (NH₄)₂S₂O₇ and H₂SO₄ which cause corrosion and plugging of the reactor and heat exchangers in the power plant. Hence there are continuing efforts in developing new catalysts.

Pillared interlayered clay (PILC) is a unique two-dimensional zeolite-like material known in the art. Because of its large pores, pillared clays have been evaluated as a possible replacement for zeolite as the catalyst for fluid catalytic cracking (FCC) which operates at near 700° C. with high steam concentration. However, pillared clays were found not to be suitable due to excessive carbon deposition and the limited hydrothermal stability of the pillared clay structure. Pillared clays have also been studied for catalyzed alcohol dehydration, alkylation and other acid catalyzed reactions. Pillared clays have also been evaluated for selective catalytic reduction of NO_x, as described in U.S. Pat. No.

5,415,850. Specifically, the '850 patent discusses pillared clay composition doped with certain concentrations of certain metals. While such reported pillared clay catalysts are useful, there is a need in the industry to continue development of catalysts that exhibit improved catalytic activity for selective catalytic reduction of NO_x.

OBJECTS AND SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide an improved catalyst composition for reducing nitrogen oxide emissions.

In summary, the present invention described herein are metal ion exchanged pillared interlayered clay catalysts. More particularly, the present invention provides a catalyst for selective catalytic reduction of nitrogen oxide compounds with ammonia comprising a composition of one or more pillared interlayered clays, one or more metal ions exchanged with the pillared interlayered clays, and one or more promoter ions exchanged with the pillared interlayered clays. Specifically, the pillared interlayered clay (PILC) catalysts of the present invention include Fe³⁺, Cr³⁺, Mn²⁺, Co²⁺, Cu²⁺, and Ni²⁺ exchanged Al₂O₃-PILC, TiO₂-PILC, ZrO₂-PILC, SiO₂-PILC and Fe₂O₃-PILC catalysts. These ion-exchanged PILCs are further promoted by rare earth metals, such as Ce, La, Pr, Tb and Nd. These pillared clay catalysts of the present invention show remarkable activity for the SCR reaction. Of significant advantage, as compared to prior art commercial catalysts, the pillared clay catalysts of the present invention yield higher activity, reduce the SO₂ oxidation of SO₃ by up to about 85%, and yield substantially less undesirable N₂O.

BRIEF DESCRIPTION OF THE DRAWINGS

Additional objects and advantages of the present invention will become apparent in reading the detailed description of the invention and the claims, and with reference to the figures, in which:

FIG. 1 is a graph showing the catalytic activity of NO reduction by NH₃ on Cr³⁺, Fe³⁺, Cu²⁺, Mn²⁺, Co²⁺, and Ni²⁺ ion-exchanged Al₂O₃-pillared laponites catalysts according to one embodiment of the present invention. The reaction conditions are: 0.3 g catalyst, [NO]=[NH₃]=1000 ppm, [O₂]=2%, He=balance, total flow rate=500 ml/min and GHSV=75 000 l/h.

FIG. 2 is a graph illustrating product selectivity as a function of temperature for N₂ (solid symbols) and N₂O (open symbols) for NO reduction by NH₃, on Cr³⁺, Fe³⁺, Cu²⁺, Mn²⁺, Co²⁺, and Ni²⁺ ion-exchanged Al₂O₃-pillared laponite catalysts according to the present invention. Reaction conditions are the same as in FIG. 1.

FIG. 3 shows catalytic activity of NO reduction by NH₃ on Fe—TiO₂-PILC, 1.0% CeO₂/Fe—TiO₂-PILC, and Ce—Fe—TiO₂-PILC catalysts according to another embodiment of the present invention and is compared with a conventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalyst in the absence of H₂O and SO₂. The reaction conditions are: 0.2 g catalyst (except 0.1 g for Ce—Fe—TiO₂-PILC), [NO]=[NH₃]=1000 ppm, [O₂]=2%, He=balance and total flow rate=500 ml/min.

FIG. 4 demonstrates the product selectivity for N₂ (solid symbols) and N₂O (open symbols) for NO reduction by NH₃ on Fe—TiO₂-PILC, 1.0% CeO₂/Fe—TiO₂-PILC, and Ce—Fe—TiO₂-PILC catalysts according to one embodiment of the present invention, and compared with a con-

ventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalyst in the absence of H₂O and SO₂. Reaction conditions are the same as in FIG. 3.

FIG. 5 is a graph showing the catalytic activity of NO reduction by NH₃ on Fe—TiO₂-PILC, 1.0-% CeO₂/Fe—TiO₂-PILC, and Ce—Fe—TiO₂-PILC catalysts according to another embodiment of the present invention, and compared with a conventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalyst in the presence of H₂O and SO₂. The reaction conditions are: 0.2 g catalyst (except 0.1 g for Ce—Fe—TiO₂-PILC), [NO]=[NH₃]=1000 ppm, [O₂]=2%, [H₂O]=8%, [SO₂]=1000 ppm. He=balance and total flow rate=500 ml/min.

FIG. 6 is a graph illustrating product selectivity for N₂ (solid symbols) and N₂O (open symbols) for NO reduction by NH₃ on Fe—TiO₂-PILC, 1.0% and CeO₂/Fe—TiO₂-PILC catalysts according to the present invention and compared with conventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalysts in the presence of H₂O and SO₂. Reaction conditions are the same as in FIG. 5.

FIG. 7 is a graph showing the effect of time on NO_x conversion of the 1.0% CeO₂/Fe—TiO₂-PILC catalyst in the presence of H₂O and SO₂. The reaction conditions are: T=375° C., 0.2 g catalyst, [NO]=[NH₃]=1000 ppm, [O₂]=2%, [H₂O]=8%, [SO₂]=1000 ppm, He=balance, total flow rate=500 ml/min and GHSV=113 000 l/h.

DETAILED DESCRIPTION OF THE INVENTION

The catalyst composition of the present invention is comprised of metal ion exchanged pillared interlayered clays (PILC), and mixtures thereof. Pillared interlayered clays finding use in the present invention include laponites, bentonites, smectites and phyllosilicates. Metals suitable for exchange with said PILCs include Fe³⁺, Cr³⁺, Mn²⁺, Co²⁺ and Ni²⁺. Copper (Cu²⁺) may also be used. Additional metals suitable for exchange include V³⁺, V²⁺ and VO²⁺.

Preferably, the PILCs are pillared with alumina or titania, specifically Al₂O₃-PILC or TiO₂-PILC. ZrO₂, SiO₂ and Fe₂O₃ pillared clays are also included. More specifically, pillared interlayered clay catalyst compositions of the present invention include Fe³⁺, Cr³⁺, Cu²⁺, Mn²⁺, Co²⁺ and Ni²⁺ exchanged with Al₂O₃-PILC, TiO₂-PILC, ZrO₂-PILC, SiO₂-PILC or Fe₂O₃-PILC.

The metal ions may be separately exchanged with the pillared clays, or a combination of one or more metal ions may be exchanged. Specific examples include but are not limited to: Fe—TiO₂-PILC, Ce—Fe—TiO₂-PILC, Fe—Al₂O₃-PILC, Cr—Al₂O₃-PILC, Cu—Al₂O₃-PILC, CeO₂/Fe—TiO₂-PILC. Preferably the catalyst of the present invention will exhibit a metal exchange level (in percent of ion exchanges) in the range approximately 10% to 400%, more preferably in the range of approximately 100% to 300%, with a metal exchange level of approximately 200% being most preferred. Of particular advantage, the present invention uses a rare earth metal promoter (or dopant). Preferably, cerium, such as CeO₂, is used as a promoter which enhances preparation of the catalyst and also increases the longevity of the catalysts. Other active promoters include oxides of La, Pr, Tb, Nd, Sm, Gd, and mixtures thereof. The amount of promoters is in the range of approximately 0.1–4.0% wt., with a range of approximately 1–2% wt. being preferred.

Fe³⁺-exchanged pillared clays were found to be the most active. In addition, the N₂/N₂O product selectivity is substantially higher with the catalyst of the present invention than that of the conventional catalysts. The catalytic activity

of Fe—TiO₂-PILC can be further improved by the addition of the promoter, preferably a small amount of cerium ions or cerium oxide or other rare earth metals. H₂O and SO₂ increase both the activity and the product selectivity to N₂. Moreover, compared to the conventional V₂O₅-WO₃/TiO₂ catalyst, the catalysts of the present invention show substantially lower activities for SO₂ oxidation to SO₃ under the same reaction condition and in particular, the Fe—TiO₂-PILC catalyst of the present invention shows lower activities of up to about 85% for SO₂ oxidation to SO₃ as compared to conventional catalysts. The catalysts of the present invention show good stability, for example an 100-hour run in the presence of H₂O and SO₂ for the CeO₂/Fe—TiO₂-PILC catalyst showed no decrease in activity.

The metal ion exchanged pillared interlayered clays of the present invention were prepared using ion exchange procedures. In one embodiment, delaminated Al₂O₃-pillared laponite was obtained from Laporte Industries, Ltd. The BET N₂ surface area and average pore diameter (measured with a Micromeritics ASAP 2010 micropore size analyzer) were 365 m²/g and 3.2 nm, respectively. In each experiment, two grams of the delaminated Al₂O₃-pillared laponite was added to 200 ml of 0.05 M Fe (NO₃)₃, Cr(NO₃)₃, Cu (CH₃CO₂)₂, Mn(CH₃CO₂)₂, Co(NO₃)₂, or Ni(NO₃)₂ solution with constant stirring. The mixtures were kept at 50° C. for 6 hours and then the particles were filtered and washed with deionized water. The exchange process was repeated three times. The obtained solid samples were first dried at 120° C. in air for 12 hours, then calcined at 400° C. for 6 hours. The samples were finally ground to 60–140 mesh. TiO₂-PILC was synthesized as follows. The starting clay was a purified montmorillonite, i.e., a purified-grade bentonite powder from Fisher Company, with particles less than or equal to 2 μm. The pillaring agent, a solution of partially hydrolyzed Ti-polycations, was prepared by first adding TiCl₄ into a 2 M HCl solution. The mixture was then diluted by slow addition of deionized water with constant stirring to reach a final Ti concentration of 0.82 M. The final concentration of HCl was 0.6 M in the preparation. The solution was aged for more than 8 hours at room temperature prior to its use. Eight grams of bentonite was dispersed in 2.0 L of deionized water and the slurry was stirred for 5 hours. The pillaring solution was slowly added into the suspension of clay with vigorous stirring until the amount of pillaring solution reached that required to obtain a 10 mmolTi/g clay. The resulting product was left in contact with the solution for 18 hours. Subsequently, the clay particles were separated by vacuum filtration and washed with deionized water until the washing liquid was free of chloride ions as indicated by using the silver nitrate test. The sample was dried at 120° C. for 12 hours and then calcined at 350° C. for 12 hours. The BET surface area and average pore size of the TiO₂-PILC were 316 m²/g and 3.3 nm, respectively. Iron ion-exchanged TiO₂-PILC catalysts of the present invention were prepared according to the procedure described above. Cerium doped Fe—TiO₂-PILC catalyst compositions in accordance with another embodiment of the present invention were prepared by using the incipient wetness impregnation method with cerium nitrate as the cerium precursor. In yet another embodiment of the invention, Ce—Fe—TiO₂-PILC catalysts were prepared by the following procedure: 2 grams TiO₂-PILC was exchanged with cerium ions (using 200 ml 0.02 M Ce(NO₃)₃ solution) for 20 hours, then exchanged with 0.05 M Fe(NO₃)₃ solution for 6 hour and repeated twice at room temperature.

In addition to the pillared clay catalysts of the present invention, conventional V₂O₅—WO₃/TiO₂ catalysts

(4.4%V₂O₅-8.2%WO₃/TiO₂) were tested for comparison. The catalysts of the present invention were prepared by incipient wetness impregnation as previously described. The V₂O₅-WO₃/TiO₂ catalyst had the same composition and surface area as a European commercial SCR catalyst as described by Tuentner et al. Also, this catalyst had nearly identical SCR activity and behavior as that of the same conventional SCR catalyst made by a major catalyst manufacturer.

The catalytic activity was evaluated by SCR activity measurements carried out in a fixed-bed quartz reactor. The reaction temperature was controlled by an Omega (CN-2010) programmable temperature controller. About 0.2 g or 0.3 g of sample was used in the experiments. Flue gas was simulated by blending different gaseous reactants. Two sets of flow meters were used to control the flow rates of the individual reactants. High flow rate gases (i.e., He, NH₃/He, or NO/He) were controlled by rotameters, whereas the low flow rate gases (i.e., SO₂, O₂) were controlled by mass flow meters (FM 4575 Linde Division). The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm NH₃, 2% O₂, 1000 ppm SO₂ (when used), 8% water vapor (when used), and balance He. The total flow rate was 500 ml/min (ambient conditions). The premixed gases (1.01% NO in He, 0.98% in NH₃ in He, and 0.99% SO₂ in He) were supplied by Matheson Company. Water vapor was generated by passing He through a heated gas-wash bottle containing deionized water. The tubings of the system were wrapped with heating tapes to prevent the formation and deposition of ammonium sulfate or ammonium nitrate. The NO and NO₂ concentrations were continuously monitored by a chemiluminescent NO/NO_x analyzer (Thermo Electron Corporation, Model 10). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap containing phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. The products were also analyzed by a gas chromatograph (Shimadzu, 14A) at 50° C. with 5A molecular sieve column for N₂ and Porapak Q column for N₂O. Hence the nitrogen balance and the product selectivity for N₂ and N₂O could be obtained.

To measure the amount of SO₃ from SO₂ oxidation during SCR reaction, a conventional wet analysis method was adopted. With the same reactor used for measuring the catalyst SCR activity, the effluent was bubbled through a solution containing BaCl₂ and HCl, where SO₃ was quantitatively captured and precipitated as BaSO₄. The precipitate was collected on an ashless filter paper which was burned along with the precipitate in a crucible, so the amount of the precipitate was accurately measured.

The following results were obtained:

SCR Catalytic Activity on Ion-exchanged Al₂O₃-pillared Laponites

The catalysts compositions of the present invention containing Fe₂O₃, Cr₂O₃, Co₃O₄, NiO, MnO_x or CuO showed high activities for the SCR reaction. Thus, the protons (H⁺) on the pillared clays were exchanged by the cations of these transition metals as potential catalysts. Ion-exchanged Al₂O₃-pillared laponite samples were prepared and the SCR activities on these catalysts are shown in FIG. 1, a graph of NO_x conversion as a function of temperature. Under the conditions of 1000 ppm NO, 1000 ppm NH₃, 2% O₂ and gas hourly space velocity (GHSV)=75 000 l/h, Co²⁺ and Ni²⁺ exchanged Al₂O₃-pillared laponite samples showed little activity in the reduction of NO_x by NH₃. A moderate activity was obtained on Mn²⁺-exchanged Al₂O₃-PILC catalyst in the temperature range of 200–400° C. Fe—Al₂O₃-PILC,

Cr—Al₂O₃-PILC and Cu—Al₂O₃-PILC were found to yield high NO_x conversions for this reaction. These results suggest that metal cations in the Al₂O₃-PILC play an important role for the reduction of NO_x. The nitrogen balance in this work was better than 95%. The maximum NO_x conversion on the Cr—Al₂O₃-PILC catalyst was obtained at 300–325° C. whereas that for Fe—Al₂O₃-PILC occurred at 375° C. As shown in FIG. 2, high selectivities for N₂O product were obtained on the Cr³⁺-exchanged Al₂O₃-PILC catalyst. The selectivity of N₂O reached approximately 40% at 400° C. While on the other pillared clay catalysts, the selectivities for N₂O were lower than 10% (i.e., the selectivities for N₂ were more than 90%) at 200–400° C. The product selectivity for N₂ decreased according to the sequence: Fe—Al₂O₃-PILC ≈ Mn—Al₂O₃-PILC > Cu—Al₂O₃-PILC >> Cr—Al₂O₃-PILC. This result was consistent with the previous studies reported in the literature that no significant amount of N₂O was formed on Fe₂O₃ catalyst, while a large amount of N₂O (along with N₂) was formed on Cr₂O₃ doped catalyst (Cr₂O₃ existed as crystalline α-Cr₂O₃, not as amorphous form).

SCR Catalytic Activity on Fe—TiO₂-PILC

Of particular advantage the Fe³⁺-exchanged Al₂O₃-pillared laponite showed good NO_x reduction activity and high selectivity for N₂ formation, thus we further investigated the catalytic performance of Fe³⁺-exchanged TiO₂-pillared bentonite for the SCR reaction. A conventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalyst was also used as a control for comparison. Under the conditions of 1000 ppm NO, 1000 ppm NH₃, 2% O₂ and GHSV=113 000 l/h, the Fe—TiO₂-PILC catalyst composition of the present invention showed high NO_x conversions at 250–450° C. as illustrated in FIG. 3. The NO_x conversion increased with temperature at first, passing through a maximum at 375° C., then decreased slightly at higher temperatures. At above 350° C., the activities of the Fe—TiO₂-PILC catalyst were better than those of the conventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalyst. When 1.0%CeO₂ was doped on the Fe—TiO₂-PILC sample, the activities for NO_x reduction were further increased. This indicated that cerium oxide played an important promoting role in the SCR reaction on the Fe—TiO₂-PILC catalyst. The Ce—Fe—TiO₂-PILC catalyst of the present invention showed the best activities for NO_x conversion at higher temperatures, although only half the amount of catalyst was used in this work. As shown in FIG. 4, the selectivities for N₂ on the three Fe—TiO₂-PILC catalysts were both significantly better than those of the conventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalyst, especially at higher temperatures. It is also significant to notice the wider temperature window of the pillared clay catalyst, especially at 400–450° C.

Due to the large amount of water vapor and sulfur dioxide (along with NO_x, O₂ and other gases) in the combustion gases from stationary sources, resistance to H₂O and SO₂ is an important criteria for catalysts used in the SCR reaction. Accordingly, the effects of H₂O and SO₂ on the catalytic performance of the catalyst compositions of the present invention, in particular three Fe—TiO₂-PILC catalysts, were studied and compared to a conventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalyst. After 8% H₂O and 1000 ppm SO₂ were added to the reactants, the NO_x conversions decreased at low temperatures (below 325° C.) on all the catalysts (comparing FIG. 5 with FIG. 3). At above 325° C., H₂O and SO₂ did not influence the activities of the conventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalyst for the SCR reaction. In contrast, however, on the three Fe—TiO₂-PILC catalysts of the present invention, NO_x conversions increased at above

325° C. in the presence of H₂O and SO₂. These results also indicated that the three Fe—TiO₂-PILC catalysts of the invention were much more active than the conventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalyst, for the SCR reaction in the presence of H₂O and SO₂. One possible theory is that both sulfated iron oxide and sulfated titanium oxide are known as solid superacid. When H₂O and SO₂ were added to the reactants, some SO₂ was oxidized to SO₃ by O₂ at the SCR temperatures and thus led to the formation of sulfate ions on the catalysts. This would increase the acidity of the catalysts containing iron and titania and thus give rise to an increase in the catalytic activity, because Brønsted acidity is important for the SCR reaction. H₂O and SO₂ also increased the product selectivities to N₂ slightly on the three catalysts of the invention, which may be attributed to a decrease of NH₃ oxidation by O₂.

Another important criteria for catalyst performance is the effect of time-on-stream on the SCR activity which is the time a catalyst is exposed to the gas stream. The effect of time-on-stream on the SCR activity of NO_x by NH₃ in the presence of H₂O and SO₂ for a catalyst composition of the present invention containing 1.0% CeO₂/Fe—TiO₂-PILC is shown in FIG. 7. As shown the 1.0%CeO₂/Fe—TiO₂-PILC is a stable catalyst in the SCR reaction. During 100 hours on stream at 375° C., under the conditions of 1000 ppm NO, 1000 ppm NH₃, 2% O₂, 8% H₂O, 1000 ppm SO₂ and GHSV=113 000 l/h, the NO_x conversion remained at ca. 96–97%, and the selectivity to N₂ was about 99%. No decrease in the activity and product selectivity were detected.

Oxidation of SO₂ to SO₃ causes severe problems for the SCR reaction due to the formation of sulfuric acid, ammonium sulfate and other compounds. Conventional vanadia-based catalysts have a high SO₂ oxidation activity, which has been a major concern in SCR operations. Efforts have been made to either add certain oxides (such a WO₃ or GeO₂) to the V₂O₅ catalyst or to use non-V₂O₅ catalysts for the purpose of decreasing SO₂ oxidation activity while maintaining high NO_x reduction activity. To test the SO₂ oxidation activity of the catalyst compositions of the present invention, the wet chemical method described in the foregoing was used to quantitatively measure the amounts of SO₃ generated in the reaction effluents. SO₂ conversions were obtained at 375° C. under the conditions of 1000 ppm NO, 1000 ppm NH₃, 2% O₂, 8% H₂O, 1000 ppm SO₂ and GHSV=113 000 l/h. The conversions for SO₂ to SO₃ were 2.1%, 2.0%, 1.2% and 8.0%, respectively, for the Fe—TiO₂-PILC, 1.0%CeO₂/Fe—TiO₂-PILC and Ce—Fe—TiO₂-PILC of the present invention, and a conventional 4.4%V₂O₅-8.2%WO₃/TiO₂ catalysts. The catalysts containing iron yield much lower SO₃ than the V₂O₅-based catalyst. Results by Clark et al., in their study of alumina supported from oxide and vanadium oxide catalysts, also showed that Fe₂O₃ was less active in SO₂ oxidation than V₂O₅. The low SO₂ oxidation activity is another significant advantage exhibited by the Fe³⁺-exchanged TiO₂-PILC catalyst of the present invention over the conventional V₂O₅-WO₃/TiO₂ catalyst.

Comparison of SCR Activity of the Catalysts

The selective catalytic reduction activity exhibited by a catalyst is an important factor. The SCR activity can be represented quantitatively by a first-order rate constant (k), since the reaction is known to be first order with respect to NO (under stoichiometric NH₃ conditions) on a variety of metal oxides. By assuming a plug flow reactor (in a fixed bed of catalyst) and free of diffusion limitation, the rate constant can be calculated from the NO_x conversion (X) by:

$$k = - \frac{F_0}{[NO]_0 W} \ln(1 - X) \tag{1}$$

where F₀ is the molar NO feed rate, [NO]₀ is the molar NO concentration at the inlet (at the reaction temperature), and W is the catalyst amount (g). According to the data shown in FIGS. 1, 3 and 5, the first-order rate constants of the SCR reaction on the above catalysts were calculated. The rate constants are compared in Table 1 below.

TABLE 1

Catalyst	First-order rate constants of the catalysts.					
	Rate constant (k, cm ³ /g/s) without H ₂ O and SO ₂			Rate constant (k, cm ³ /g/s) with H ₂ O and SO ₂		
	350° C.	375° C.	400° C.	350° C.	375° C.	400° C.
Fe—Al ₂ O ₃ -PILC	123	139	123	—	—	—
Cr—Al ₂ O ₃ -PILC	118	91	62	—	—	—
Cu—Al ₂ O ₃ -PILC	93	81	61	—	—	—
Fe—TiO ₂ -PILC	185	200	192	218	255	292
1.0%CeO ₂ /Fe—TiO ₂ -PILC	200	229	217	261	318	395
Ce—Fe—TiO ₂ -PILC	260	408	464	336	510	606
4.4% V ₂ O ₅ -8.2% WO ₃ /TiO ₂ Commercial V ₂ O ₅ Catalyst (Company X) ^a	177	192	192	177	192	192

^aData was obtained from J. P. Chen et al., "Iron Oxide and Chromia Supported on Titania-Pillared Clay for Selective Catalytic Reduction of Nitric Oxide with Ammonia", J. Catal. 151, 135 (1995). Reaction conditions: [NO] = [NH₃] = ppm, [O₂] = 2%, [H₂O] = 8% (when used), [SO₂] = 1000 ppm (when used), He = balance and total flow rate = 500 ml/min.

In the absence of H₂O and SO₂, the rate constants for various catalyst compositions of the present invention were found to increase in the order of Cu—Al₂O₃-PILC<Cr—Al₂O₃-PILC<Fe—Al₂O₃-PILC<4.4%V₂O₅-8.2%WO₃/TiO₂<Ce—TiO₂-PILC<1.0%CeO₂/Fe—TiO₂-PILC<Ce—Fe—TiO₂-PILC. The Ce—Fe—TiO₂-PILC catalyst was the most active catalyst for the SCR reaction. When H₂O and SO₂ were added, the activities of the three Fe—TiO₂-PILC catalysts were further increased. The Ce—Fe—TiO₂-PILC catalyst was more than three times as active as the conventional vanadia catalyst under the same conditions with SO₂ and H₂O at 400° C.

The Fe³⁺-exchanged titania-pillared clay catalysts of the present invention (promoted by cerium) showed very high NO_x conversion in the SCR reaction by ammonia, which were up to more than three times as active as the commercial V₂O₅-WO₃/TiO₂ catalyst. The pillared clay catalysts also had a higher N₂/N₂O product selectivity and a substantially lower activity for SO₂ oxidation to SO₃ than the commercial catalyst. A 100-hour run in the presence of H₂O and SO₂ for the 1.0% CeO₂/Fe—TiO₂-PILC catalyst showed no reduction in activity.

As taught by the foregoing description and examples, a superior pillared clay catalyst for selective catalytic reduction of nitrogen oxides is provided by the present invention. The foregoing description of specific embodiments and examples of the invention have been presented for the

purpose of illustration and description, and although the invention has been illustrated by certain of the preceding examples, it is not to be construed as being limited thereby. They are not intended to be exhaustive or to limit the invention to the precise forms disclosed, and obviously many modifications, embodiments, and variations are possible in light of the above teaching. It is intended that the scope of the invention encompass the generic area as herein disclosed, and by the claims appended hereto and their equivalents.

- We claim:
1. A catalyst for selective catalytic reduction of nitrogen oxide compounds with ammonia, comprising:
 - a composition of one or more pillared interlayered clays (PILC);
 - one or more metal ions exchanged with said pillared interlayered clays; and
 - one or more promoter ions exchanged with said pillared interlayered clays.
 2. The catalyst of claim 1 wherein said pillared interlayered clays are selected from the group consisting of Al₂O₃-PILC, TiO₂-PILC, ZrO₂-PILC, SiO₂-PILC and Fe₂O₃-PILC.
 3. The catalyst of claim 1 wherein said metal ions are selected from the group consisting of Fe³⁺, Cr³⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, V³⁺, V²⁺, VO²⁺ and mixtures thereof.
 4. The catalyst of claim 1 wherein said promoter ions are selected from the group consisting of Ce, La, Pr, Nd, Sm, Gd, Tb and mixtures thereof.

5. The catalyst of claim 1 wherein the percent of metal ions exchanged is in the range of approximately 10% to 400%.
6. The catalyst of claim 1 wherein the percent of metal ions exchanged is in the range of approximately 100% to 300%.
7. The catalyst of claim 1 wherein the percent of metal ions exchanged is approximately 200%.
8. The catalyst of claim 1 wherein said promoter ions are present at a concentration in the range of approximately 0.1–4% wt.
9. The catalyst of claim 8 wherein said promoter ions are present at a concentration in the range of approximately 1–2% wt.
10. A catalyst for selective catalytic reduction of nitrogen oxide compounds with ammonia wherein said catalyst is selected from the group consisting of:
 - Fe—Al₂O₃-PILC, Cr—Al₂O₃-PILC, Cu—Al₂O₃-PILC, Fe—TiO₂-PILC, CeO₂/Fe—TiO₂-PILC and Ce—Fe—TiO₂-PILC.
11. The catalyst of claim 10 wherein said catalyst is Ce—Fe—TiO₂-PILC.
12. The catalyst of claim 10 wherein said catalyst is 1.0% CeO₂/Fe—TiO₂-PILC.

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